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13. ABSTRACT *(Maximum 200 Words)*

A broad array of apparatus for fabricating and characterizing newly-developed photorefractive polymer materials has been purchased with the funds from this DURIP grant. While these pieces of equipment emphasize the infrared range of the spectrum, instruments have also been acquired which measure thermal and dielectric properties of this new and growing class of high-performance materials. A crucially important study of the trapping states in a major class of photorefractive polymers has already been completed, in which the concentration of the fullerene anion has been measured with a near-infrared spectrometer acquired through this grant. The concentration of fullerence anion correlates well with the all-important photorefractive trap density determined by two-beam-coupling experiments, proving that the anion is the primary trapping species. This information will allow careful optimization of future photorefractive polymer materials. At the same time, a full infrared-capable photorefractive polymer characterization system has been constructed, and this apparatus will be applied to understand and optimize photorefractive behavior in a wide array of new materials.

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FINAL TECHNICAL REPORT

INFRARED PHOTOREFRACTIVE POLYMER CHARACTERZATION SYSTEM

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1. Equipment Acquired Through This Defense University Instrumentation Program Grant:

The equipment acquired is listed in detail in the following table:

Item	Supplier	Name	Amount - Costs Include Tax
Total Award			**$154,745**
Matching funds from UCSD			**$48,000**
Total			**$202,745**
Fabrication of Near-Infrared Photorefractive Characterization System, including optics, mounts, diode laser, detectors, amplifier, controller, interface	Newport, Oriel, Melles Griot, New Focus, ILX Lightwave, Stanford Research, Hewlett-Packard, National Instruments, Pulnix, EGG, Uniblitz	n/a	$52,502
Near-IR Spectrophotometer with capability to 1.5 microns	Perkin-Elmer	Lambda 19, with controller and software	$47,194
Light Scattering System with Molecular Weight Capability	Wyatt Technology Corp.	DAWN DSP, multi-angle with Aurora software	$43,400
Thermogravimetric Analyzer	TA Instruments	TGA 2050	$24,765
Dielectric Analysis System	Solartron	1296 Dielectric Interface with Corrware	$24,884
Glove Box	Used unit acquired from Prof. J. O'Connor		$10,000
NET			$0

The purchased equipment differs only slightly from that in the original budget in the proposal. The near-ir spectrometer with full capability and the light scattering system both cost more than the original quote. In addition, it became clear to us that proper characterization of our new polymers and composites required assessment not only with a Differential Scanning Calorimeter (purchased separately), but also with thermogravimetric analysis (TGA). This analysis tool allows quantification of solvent content and weight loss, which are especially important in improving sample stability and longevity. Accordingly, a TGA compatible with our DSC was added, and the refractometer was deleted. We identified another group (Prof. Perrin)

who has allowed us to borrow this item for our use. In addition, we were able to obtain a used glove box, and we were able to reduce the cost of the Infrared Characterization System by purchasing several items from other sources.

2. Summary of Research Projects Completed and/or In Progress:

One of the major items purchased, the *Near-IR Spectrometer*, has already produced astounding results (see publication 1 below). By purchasing a complete unit from Perkin-Elmer which spans from the uv to the near-infrared, we were able to perform a detailed trapping study on photorefractive polymers for the first time as follows. We often utilize C_{60} as a sensitizer for our high-performance composite samples, which have shown high gain coefficient (~200 cm^{-1}), high gain factor (500x single-pass), and even high speed (4 ms at 1 W/cm^2 – see publication 3). We realized that the C_{60} anion is crucial to the trapping dynamics, and showed that *optical measurement of the sample absorption at 1.08 microns wavelength can be used to follow the C_{60} anion concentration in as-made PR polymer samples.* This measurement was compared with a determination of the PR trap density by fitting the dependence of the gain coefficient on applied electric field as usual. The two measurements agreed closely, *proving that the C_{60} anion provides the principal trapping center for photorefractivity in these materials.* By additional spectroscopic measurements as a function of time and irradiation at 647 nm, we showed that the nonlinear optical chromophore acts as a compensator, allowing a background concentration of C_{60} anion to build up with time.

The significance of these results is three-fold. First, the principal trapping sites have been identified. Second, the compensating centers have been identified, and they are likely to play a role in the time response of the samples. Third, these useful facts provide a framework for the rational design of new PR polymers, as the NLO chromophore is now no longer a passive component, but its energy levels must be taken into account in controlling the all-important photorefractive trap density in the final materials.

The *Thermogravimetric Analyzer* has been purchased and received. This instrument has been used to analyze the thermal stability and solvent content of several polymer samples. This instrument has been particularly useful in analyzing the source of difficulty when samples have proved challenging to fabricate. By allowing determination of thermal stability at the temperatures used in oven drying, we were able to assess the ability of the components to tolerate the drying temperatures, and to modify the fabrication protocol appropriately.

The *Solartron Dielectric Analysis System* has been purchased and received. This device has been used to obtain the frequency dependence of the dielectric constant in a variety of polymer composite samples. To date, this device has provided us with two useful pieces of information. First we were able to obtain the dielectric constant at a very low frequency (1 Hz). This parameter is critical in calculating the number density of photorefractive traps as mentioned above. The other useful information provided was in the shape of the dielectric relaxation curves obtained. We observed a persistent dispersion down to very low (mHz) frequencies, which informs us that polymer and/or sample component dynamics (perhaps polymer creep) still occurs on long time scales. These issues will be analyzed more thoroughly in the future.

The *Near Infrared Photorefractive Characterization System* consists of a large number of smaller optical components, mounts, positioning systems, electronics, and laser devices. These components are being fabricated into a setup that would be capable of two- and four-wave

mixing in the infrared with easily adjustable parameters such as grating spacing, write/read wavelength and intensity, and electric field. This type of measurement allows us to flexibly determine the photorefractive properties and performance of each sample. Specifically, the two beam coupling gain coefficient, diffraction efficiency, grating phase shift, maximum index modulation and grating response time can be measured as a function of the experimental parameters. We have previously demonstrated in the visible that with this knowledge, we obtain a detailed picture of the mechanisms of photorefractivity, which allows more efficient materials to be created.

All of the required components to fabricate this system were ordered early in the grant year. Unfortunately several parts of this apparatus required somewhat large lead time, such as laser diodes at particular infrared wavelengths and custom parts that we had constructed for us at a local machine shop. We have recently received all of the necessary parts for the setup. This device is now in the final stages of alignment and checkout, and should be capable of making measurements on new infrared-sensitive PR polymers soon.

Regarding the *Light Scattering System*, we felt that incorporation of transition metal ions into PR polymers would provide a means of sensitization for photoconductivity in the near-infrared, and may provide new functionality for optical nonlinearity and transport. We have therefore applied our "metal complexes as synthetic building blocks" approach for the synthesis of Ru(II)-containing polymers as described in the original proposal. These novel polymers have been characterized by spectral means as well as by multi-angle light scattering.

The Wyatt Technology DAWN DSP multi-angle light scattering detector has been installed and aligned. After some experimentation with standard samples of polystyrene, the DAWN DSP has been used to asses the weight average molecular weight of the first generation of conjugated, metal-containing polymers. Initial studies were done in batch mode, which is simpler and faster than microbatch work, but moderately less accurate. Nevertheless, the results indicate that the molecular weight obtained from the light scattering analysis is in close agreement with that determined using NMR end-group analysis. In addition, the light scattering also provides information about the radius of gyration of the polymers in solution, as well as their shape. There were no apparent complications due to incident light absorption (rather than scattering) by the conjugated backbone of the polymer.

3. Recent Publications:

1. A. Grunnet-Jepsen, D. Wright, B. Smith, M. S. Bratcher, M. S. DeClue, J. S. Siegel, and W. E. Moerner, "Spectroscopic Determination of Trap Density in C_{60}-Sensitized Photorefractive Polymers," appearing in *Chem. Phys. Lett.* (1998).
2. M. S. Bratcher, M. S. DeClue, A. Grunnet-Jepsen, D. Wright, B. Smith, W. E. Moerner, and J. S. Siegel, "Synthesis of Fully-Functional Photorefractive Polymers with Net Gain: Design Strategy Amenable to Combinatorial Optimization," appearing in *J. Amer. Chem. Soc.* (1998).
3. D. Wright, M. A. Diaz-Garcia, J. D. Casperson, M. DeClue, and W. E. Moerner, "High Speed Photorefractive Polymer composites," submitted to *Appl. Phys. Lett.* (1998).